Gold assay with Knudsen effusion mass spectrometry

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ABSTRACT

Commercial 18 carat (ct) gold alloys along with pure coinage metals have been
effusion mass spectrometry. Isotopic fractionation in vapour phase and the en
were estimated for Au, Ag and Cu samples. The assaying of the gold content was
calibration with respect to standard reference alloys measured with energy disper
The accuracy of the gold determination resulted of about 1.5 wt.‰ in the ternary

1. Introduction

Nowadays, more than 75% of the global gold output is processed in the jewellery industry, which means that for international economics accurate determination (assay) of the gold content (fineness) is very significant. An ideal method of assaying should be accurate at the level of one part per mil (1‰), fast and reasonably priced. Other important factors are the size of the samples, consistency and reliability of the measurements, determination of all components, whether the method is destructive or non-destructive, etc.

The traditional cupellation (fire assay) [1] is the method used worldwide for gold determination. It is a very ancient technique mentioned even in the Bible. In its present form, cupellation remains the most accurate method available and serves as the standard technique against which all others are compared. It is covered by the ISO standard ISO 11426:1993.

In recent years, the need for fast and accurate gold assaying methods stimulated the testing of a number of modern analytical techniques such as energy dispersive X-ray fluorescence (XRF) [2,3], glow discharge and inductively coupled plasma-optical emission and mass spectrometric methods [4,5], laser-induced breakdown spectroscopy [6,7], etc. For details about th
mental techniques, applying to determinatio
the reader is addressed to the monograph of V
[8].

Energy dispersive X-ray fluorescence spe
most popularity now, finding service in both j
in assay laboratories. There are many produce
on the market. According to Ref. [9], XRF can r
content) of an alloy with an accuracy of 0.75
conditions, however typical accuracy is about
is non-destructive, determines all elements
ones (C, B, Be), but only in the near-surface
in depth. Electroplating or chemical treatm
surface composition, distort the results of XF
surements, the sample surface should be cle
and at least 3 mm in diameter. Curved surf
since the emitted X-rays are randomly scatte

Therefore, the development of novel meth
is still ongoing. Recently, SIMS and mass-re
spectrometry have been applied to the cha
trodeposited Au, Pd and Ru coatings [10], ar
gold coins [11]. These techniques are very s
advantage of sputter depth profiling within
depth, however, they are scarcely suited for
the bulk elemental content.

Knudsen (cell) effusion mass spectrometr
proved to be a powerful tool for determinati
properties of different materials, including g

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Generally, gold title is expressed in weight parts per mill (wt.‰) or in the standard units called carats (not to be confused with the weight carat equal to 200 mg and used for a variety of materials, including diamonds and pearls). Pure gold corresponds to 24 carat (ct) according to the Common Control Mark scale. Along with basic coinage metals some additional (dopant) metals like zinc, tin, nickel, etc. can be found in jewellery alloys. These additives influence the mechanical properties and coloration of alloys. Some physical and thermal properties of coinage and dopant metals are listed in Table 1.

The measurements reported in the present work were carried out with a custom-built Knudsen effusion mass spectrometer. The schematic configuration of the instrument is shown in Fig. 1.

A linear time-of-flight analyser LFT 10 with mass resolution $M/\Delta M \geq 500$ (FWHM) was developed by Stefan Kaesdorf [15]. Electron impact ionization ion source (E_{el} = 5–90 eV) is equipped with two permanent magnets ($B = 10^{-2}$ T) which guide the electron beam through the ionization zone. A two-stage extraction scheme according to Wiley–McLaren [16] compensates for the difference in the starting position of the ions. The field-free drift part has a length of 588.5 mm. For the efficient detection of heavy molecules with masses up to 1000 m/z the ions are accelerated to a maximum energy of 8 keV before hitting the detector (a two-stage microchannel plate by Burle [17] with 25 mm in active diameter). The software TOF 5.0 allows data acquisition, evaluation and treatment.

A high-temperature effusion cell HTC-40-2-220-SHM-WK with control unit CU-2404-S1-AC was developed by CreaTec Fisher [18]. The control unit contains a precise PID controller in combination with an AC power supply (max output power of 700 W). A 2 cm^3 cylindrical crucible is heated up to 2000 °C by a self supported tungsten wire. We used crucibles made in graphite (PRG). The cell temperature was measured using a calibrated W–Re (5–26%) thermocouple. The temperature stability was found to be ca. ±0.5 °C.

Metal vapours, effusing through a small cylindrical orifice of 1 mm in diameter, are collimated with a 2 mm aperture placed in the space between effusion cell and ionization chamber of the ion source. The manual shutter allows interrupting the molecular beam. The Clausing factor, k, of the effusion orifice, estimating in accordance with [19,20] as

$$k = \left[0.98441 + 0.00466\left(\frac{l}{r}\right)\right] \times \left[1 + 0.46034\left(\frac{l}{r}\right)\right]^{-1}, \qquad (1)$$

50–250 mg, about 50–60% of them initial remain into the cell after the ending of measurements were carried out over the ture range depending on the sample co maintained at a constant temperature whi range of 1–400 m/z were recorded sequen was recorded with closed shutter (denoted resulting data are calculated as a differenc estimated from the 1st to 3rd spectra and t trons of 20 eV were used in the ion sourc effusing from the cell.

3. Results and discussion

3.1. Evaporation of the pure coinage metals

Mass spectra of the positive ions meas of pure Cu, Ag and Au are shown in Fig. 2. Th ca. 100 mg. Mass resolution, $M/\Delta M$ (FWHM ^{63}Cu, ^{107}Ag and ^{197}Au, respectively. Blank s gold exhibit no peaks in the range of inter and c). For the copper sample, a peak of 64, between the isotope peaks ^{63}Cu and ^{6} in Fig. 2a with a dot line). For the silver ture higher than 1400 °C along with the at ion species Ag_2^+ were detected but in a li intensity ratio $^{107}Ag/(^{107}Ag^{109}Ag) \geq 500$ at

Fig. 3 shows the peak intensities of the and Au against the relative temperature term "peak intensity" here the pea the threshold of 5 counts. The relative tem $T_{rel} = T/T_1$, where T is the actual temperatur T_1 refers to the temperature necessary to pressure of the elements [22] (see Table 1 in the centigrade scale (°C). The introduct perature facilitates the presentation of our the graphical form.

For the copper and silver samples we me tionation in the vapour phase versus the re effusion cell. Commonly, the isotopic frac

Table 1
Physical and thermal properties of coinage and dopant metals formed commercial gold alloys

	Au	Ag	Cu	Z
Atomic number	79	47	29	3
Molecular weight (g mol^{-1})	196.97	107.87	63.55	6
Ionization energy (eV)	9.23	7.58	7.73	9
Melting point (°C) [22]	1063	961	1084	4
Temperature (°C) necessary to reach 1.33 mbar vapour pressure [22]	1707	1337	1628	4
Main isotope and its abundance ratio (%) [29]	^{197}Au/100	^{107}Ag/51.84	^{63}Cu/69.17	6

Fig. 1. General arrangement of the instrument, not to scale.

tive deviation of the measured abundance ratio of two isotopes of an element from the corresponding standard value of this ratio. The magnitude of δ is expressed per mil via

$$\delta = \left(\frac{R_{exp}}{R_{st}} - 1\right) \times 1000, \quad (2)$$

where R_{exp} and R_{st} denote the experimental and standard ratios of the heavy-to-light isotope abundances ($^{65}Cu/^{63}Cu$ and $^{109}Ag/^{107}Ag$ in our case). Hence, a negative value of the δ-parameter signifies a depletion of the heavy isotope relative to the standard.

As indicated in Fig. 4, within the limits of the experimental error (±10‰), the magnitude of the isotopic fractionation $\delta^{109}Ag$ tends to zero over all the temperature range, while the $\delta^{65}Cu$ value increases with an increasing temperature. This phenomenon could be interpreted as due to artefacts associated with the peak intensities rather than the peak masses. Heavy isotopes both of silver and, especially, of copper are less intense than the light ones (a standard abundance $R(Ag)_{st} = 0.929$ and $R(Cu)_{st} = 0.4457$). Due to the probable saturation of the detector in our experiments, it may be that with increasing temperature, and increasing total peaks intensity as well, the light copper isotope could be suppressed in a greater extent than the heavier one.

In general, the vapour pressure of isotopes depends on their masses on $(-(1/2))$ degree (see, e.g., Ref. [23]). For this reason, the heavier isotope could be depleted in vapour flux relative to the standard isotopic abundance. Quantum–mechanical calculations by Teller et al. [24] confirmed this conclusion, however, in the same publication the situation when under evaporation of the C_6D_6 and C_6H_6 mixture the vapour was enriched with the compound on base of deuterium is also discussed.

Detailed discussion of the possible sources for the isotopic fractionation in the vapour phase is beyond the scope of the present paper. At this stage, we consider isotopic fractionation measurements as a means of testing of our instrument. Therefore, we used the data shown in Fig. 4 for the temperature optimization of the effusion cell, assuming that under the minimum magnitude of the δ-parameter, the accuracy of the gold assay The optimal temperatures in our experimen coincided with T_1, i.e., with the temperatures 1 mbar vapour pressure of the pure compone

The best test for proper operation of a Kn is determination of the enthalpy of vaporiz equation in chemical thermodynamics [25] temperature to the change in the equilibriu enthalpy. It assumes that the enthalpy chang temperature range as

$$\ln(K) = -\frac{\Delta H^\circ}{R}\left[\frac{1}{T}\right] + \frac{\Delta S^\circ}{R},$$

where K is the equilibrium constant at absolu and ΔS° are the enthalpy and entropy chang is the gas constant ($R = 8.31447$ J/mol K).

For a simple vaporization reaction like A rium constant $K = p(A)$, where p is the pres a Knudsen cell. Since $p(A) \propto I(A)\cdot T$ (for detai where I is the ion intensity of A-element, the tion may be determined from the slope of $\ln(I$ reciprocal absolute temperature without kn parameters. Conversely, these extra paramet order to determine ΔS°.

The Van't Hoff plots for the main isotopes o are shown in Fig. 5. The results of the ΔH° esti temperature of the measurements are presen show there the values of ΔH° calculated at th using Ref. [26] and the currently accepted val vaporization of pure Cu, Ag and Au at room te discrepancy between our results and the lit interpreted as due to the fact that the sampl instruments is not perfectly in equilibrium fr point of view. It is likely that an error is int of the modest value of the sample-to-orifice is $s = 25–35$ (should be 10^2, at least, accordi

Table 2
Enthalpy of vaporization of pure coinage metals

Sample	Enthalpy of vaporization ΔH° (kJ mol^{-1})		
	Our experimental data	Calculated data [26]	Currently ac
Copper	365 ± 20 (1923 K)	309.8 (1900 K)	367.0 ± 0.9
Silver	260 ± 7.5 (1623 K)	261.2 (1600 K)	284.5 ± 1.3
Gold	395 ± 15 (1823 K)	343.4 (1800 K)	337.6 ± 1.2

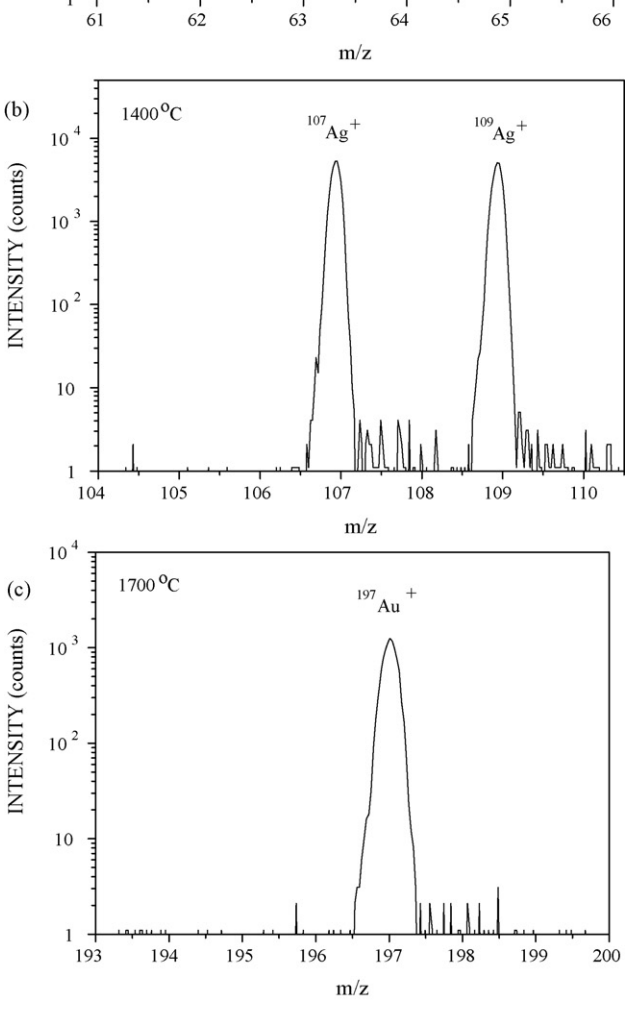

Fig. 2. Mass spectra of the positive ions measured under vaporization of pure copper (a), silver (b) and gold (c). For the Cu sample the blank spectrum registering with the closed shutter is shown too. The temperature of the effusion cell is indicated at the upper left corner of every panel.

other sources of error could be (i) the imperfect vapour-tightness of our cell that allows uncontrolled loss of analysed materials during evaporation, and (ii) a rather high pressure into the cell, well above 10 Pa, that is an upper limit of molecular flow through the cell orifice under the Knudsen effusion conditions.

3.2. Evaporation of the jewellery alloy

We studied three different commercial 18 ct gold alloys, in two samples of every alloy. The sample denoted in our experiments

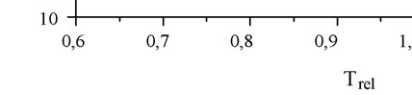

Fig. 3. Peak intensities of the main isotopes of coin
temperature. The temperature of the effusion cell is

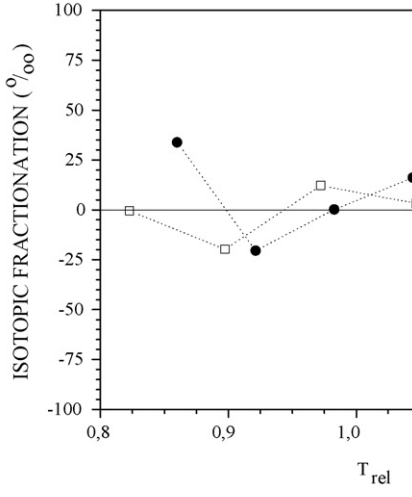

Fig. 4. Isotopic fractionation δ^{65}Cu and δ^{109}Ag me
tive temperatures. The temperature of the effusio
1400–1900 °C for copper and of 1100–1600 °C for silv

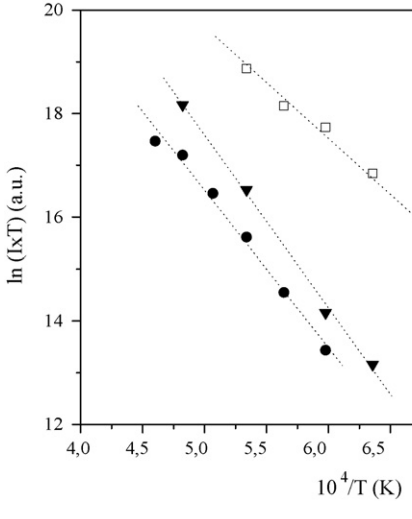

Fig. 5. The Van't Hoff plots for the main isotopes
temperature of the effusion cell is within the rang
1300–1800 °C for copper, silver and gold, respectively

determined for a LPT 10 analyser in the residual gas analysis mode. It means that the molecular beam, emerging from the effusion cell, is better localized into the space of the ionization chamber than randomly moving gas molecules, and the space focusing regime according to Wiley–McLaren scheme perfectly suits for measurements of evaporated species.

The blank spectrum of zinc (a dot line in Fig. 7a) exhibits intense features also with the closed shutter. The zinc content in the alloys is low, slightly less than 20 wt.‰, and its ionization potential is high (9.39 V). Thus, we expect to measure zinc at higher relative temperature of the effusion cell ($T_{rel} \geq 1.5$) in comparison to other components. Since our cell is not totally vapour-proof, the evaporated species effuse not only through the outlet orifice and could get to the analytical chamber around the closed shutter, especially, when the partial pressure of the component into effusion cell is very high (for Zn at 700–800 °C it reaches hundreds mbar).

3.3. Quantification on the gold alloys

The determination of the sample content is carried out by calibration with respect to standards quantified with other methods. One of the samples of every alloy is considered as a "reference sample" (Table 3), and for each component of this sample the KEMS elemental sensitivity factors were evaluated using the data presented in Fig. 5. Then, we applied these factors for quantification of another, "determined sample" belonging to the same alloy grouping and compared the results of our calculation with the data obtained by EDS (Table 4). The weight of the reference and determined samples is different in our experiments since we would like to see how this parameter influences on the accuracy of assaying.

At first, we used pure metals as standards. However, this approach yielded low precision of quantification, and vaporization of pure zinc resulted in heavy contamination the ion source and the analytical chamber.

The elemental sensitivity factor of the *i*-component is determined as

$$SF_i = \left(\frac{I}{N}\right)_i, \quad \text{counts (at. ‰)}^{-1} \tag{4}$$

where I is the peak intensity of the main isotope ions and N is the atomic concentration (per mil).

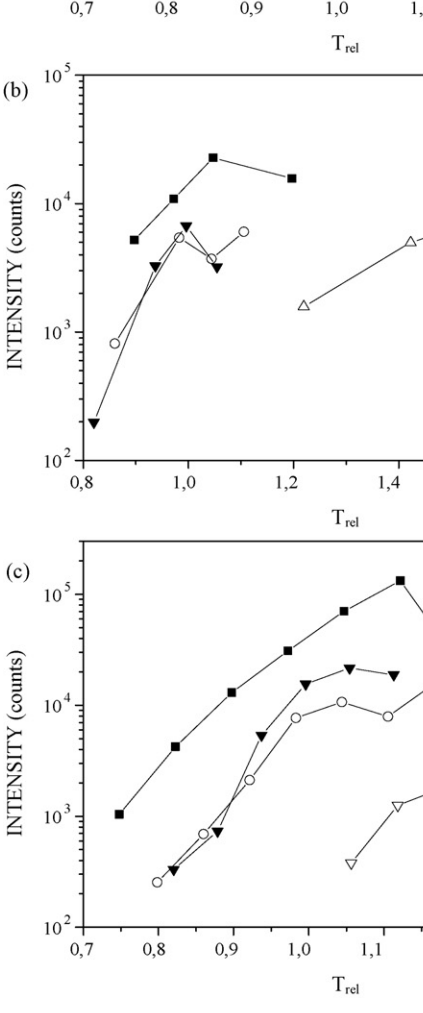

Fig. 6. Peak intensity of the main isotopes of Cu, Ag, Au, Zn temperature measured under vaporization of the commo *Alloy 2R* (b) and *Alloy 3R* (c). The temperature of the effusio range.

Table 3
Reference 18 ct gold samples: *W* is a relative weight content of the components, wt.‰; SF is a sensitivity factor, counts per at.‰

Alloy	Weight (mg)	Au		Ag		Cu		Zn	
		W	SF	*W*	SF	*W*	SF	*W*	SF
Alloy 1R	210	769.0	5.11	122	192.6	109	41.05	–	–
Alloy 2R	100	754.5	12.18	110.5	74.52	116	20.74	19	224.4
Alloy 3R	165	749.5	26.60	149	332.4	67	47.59	–	–

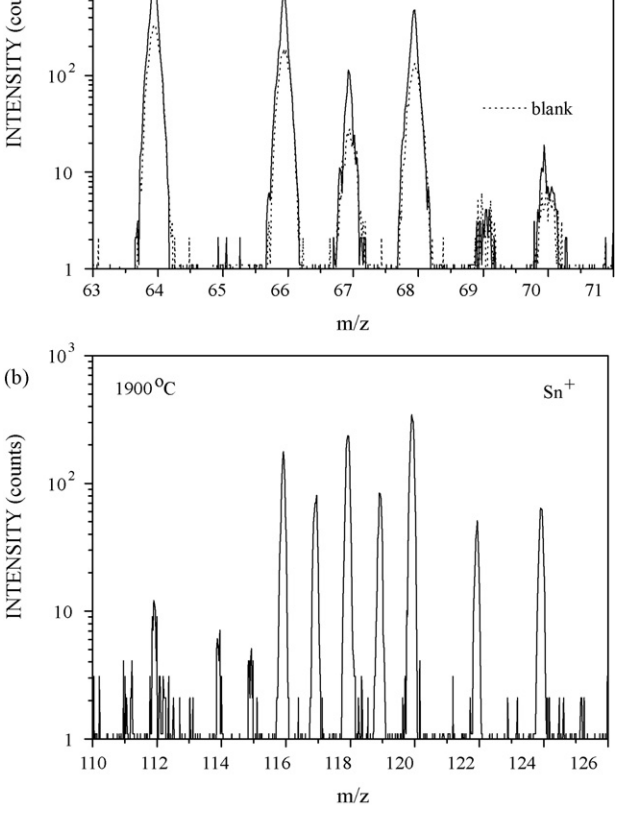

Fig. 7. Mass spectra of the positive ions of zinc (a) and tin (b) measured under vaporization of the quaternary *Alloy 2R* and *Alloy 3R*, respectively. For the zinc-contained sample the blank spectrum registered with the closed shutter is shown too. The temperature of the effusion cell is indicated at the upper left corner of every panel.

Atomic concentration and weigh content W is related by

$$N_i = \frac{W_i/M_i}{\sum_{i=1}^{n}(W/M)_i} \times 1000, \quad \text{at. ‰} \tag{5}$$

where M is the molecular weight (see Table 1) and n is the number of the components.

The recalculation of atomic concentration to weight content is performed via

$$W_i = \frac{(N \cdot M)_i}{\sum_{i=1}^{n}(N \cdot M)_i} \times 1000, \quad \text{wt. ‰} \tag{6}$$

The relative error in the determination of elemental sensitivity factors SF_i (Table 3) does not exceed ±1% for gold and silver, ± 1.5% for copper and ±2.5% for zinc and tin. The optimal temperature of the effusion cell, at which SF-values is determined, was found to

13 wt.‰ for the quaternary alloys. For Ag accuracy of determination within 25 wt.% 3 wt.‰. Since EDS also needs adequate cal depth of this technique is of 1–2 μm only, that the errors in our assaying procedure due to application of EDS as reference met

Another problem is "matrix effect". As elemental sensitivity factors exhibit varia alloys. In principle, this is known effect, ma nature of vaporization and effusion (see, e.g tion of $AlNi_3$ alloy and pure Al and Ni prese framework of our quantification approach sort of the gold alloys should be properly ca and (ii) experimental conditions during the ence and determined samples should be ic number of the commercial gold alloys is lim studied in the present work, the low title a of gold) and 8 ct (333 wt.‰) are often used with more rare 22 ct (917 wt.‰) and 23 ct

4. Summary

The present study provides a detailed ch ization of coinage metals and 18 ct gold al were carried out by means of a high-tempe mass spectrometer equipped with a linea and an electron impact ionization ion sourc topic fractionation measurements in vapo the enthalpy of vaporization for pure Au, A

Our purpose was to examine the appl priced custom-built KEMS instrument for g of the present work show that it is possib sion mass spectrometry for gold determi proper calibration involving standard refe stage, an accuracy of the gold assay wit order or better as that of XRF, at least f but our results are still inferior to cupel interesting characteristic of KEMS lies pe requires no special sample preparation be this respect, the method turns out to be mo XRF.

The following investigations and appa in progress or planned:

(1) Quantification of other commercial go for jewellery fabrication.
(2) Involving more accurate reference me the standards.
(3) Rearrangement of the instrument resu tion of the effusion cell that should

giani for his assistance in the development and assembling of the instrument, and Dr. S. Kaesdorf advising us about adjustment and optimization of LFT 10 analyser. Our thanks go to Dr. M. Caneschi for the gold alloys presented to our measurements. Also we would like to thank Mr. M. Stancampiano and Mr. R. Stancampiano, of the E. Stancampiano s.p.a. company, for their interest and support of this work. Finally, we are much obliged to the (unknown) reviewers who helped us to amend our presentation.

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